

PCT

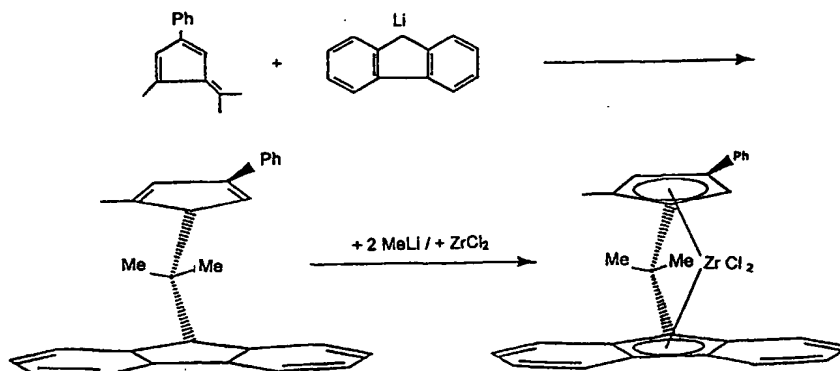
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C08F 297/00, 297/06, 297/08, 10/00, C07F 17/00		A1	(11) International Publication Number: <b>WO 99/67309</b> (43) International Publication Date: 29 December 1999 (29.12.99)
(21) International Application Number: PCT/EP99/04248 (22) International Filing Date: 18 June 1999 (18.06.99) (30) Priority Data: 98111334.3 19 June 1998 (19.06.98) EP (71) Applicant (for all designated States except US): FINA RESEARCH S.A. [BE/BE]; Zone Industrielle C, B-7181 Seneffe (Feluy) (BE). (72) Inventors; and (75) Inventors/Applicants (for US only): RAZAVI, Abbas [IR/BE]; Domaine de la Brisée, 35, B-7000 Mons (BE). HORTMANN, Kai [DE/BE]; Weidestraat, 42 B, B-1700 Dilbeek (BE). (74) Common Representative: FINA RESEARCH S.A.; Patent Dept., Zone Industrielle C, B-7181 Seneffe (Feluy) (BE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report.	

(54) Title: POLYOLEFIN PRODUCTION



(57) Abstract

A C<sub>1</sub> symmetric metallocene compound of the general formula: R'' (CpR<sub>n</sub>)(Cp'R'<sub>m</sub>) MQ<sub>p</sub> for use as a catalyst component in the production of short sequence syndiotactic/isotactic block polyolefins, wherein Cp is a substituted cyclopentadienyl; each R is independently aryl or hydrocarbyl having 1 to 20 carbon atoms, at least position 3 of Cp is substituted with aryl, at least one other position of Cp is substituted with a non-bulky substituent, and n is an integer in the range from 2 to 4; Cp' is substituted or unsubstituted fluorenyl; each R' is independently hydrocarbyl having 1 to 20 carbon atoms and m is 0 or an integer in the range from 1 to 8; R'' is a structural bridge to impart stereorigidity between Cp and Cp'; M is a metal from Group IIIB, IVB, VB or VIB; Q is a hydrocarbyl radical having 1 to 20 carbon atoms or a halogen; and p is the valence of M minus 2.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## POLYOLEFIN PRODUCTION

## FIELD OF THE INVENTION

The present invention relates to a metallocene compound for use as a catalyst component in the production of short sequence syndiotactic/isotactic block polyolefins, catalyst systems containing the metallocene compound and their use in processes for the production of such polyolefins.

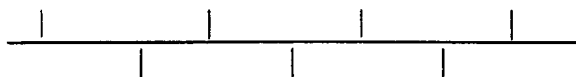
## BACKGROUND TO THE INVENTION

Olefins having 3 or more carbon atoms can be polymerised to produce a polymer with an isotactic stereochemical configuration. For example, in the polymerisation of propylene to form polypropylene, the isotactic structure is typically described as having methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer. This can be described using the Fischer projection formula as follows:



Another way of describing the structure is through the use of NMR spectroscopy. Bovey's NMR nomenclature for an isotactic pentad is ... mmmm with each "m" representing a "meso" diad or successive methyl groups on the same side in the plane.

In contrast to the isotactic structure, syndiotactic polymers are those in which the methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer. Using the Fischer projection formula, the structure of a syndiotactic polymer is described as follows:



In NMR nomenclature, a syndiotactic pentad is described as

CONFIRMATION COPY

- 2 -

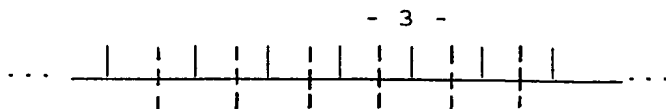
...rrrr... in which "r" represents a "racemic" diad with successive methyl groups on alternate sides of the plane.

In contrast to isotactic and syndiotactic polymers, an atactic polymer exhibits no regular order of repeating unit. Unlike syndiotactic or isotactic polymers, an atactic polymer is not crystalline and forms essentially a waxy product.

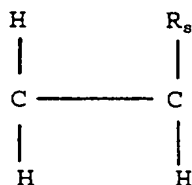
The production of syndiotactic/isotactic block polypropylene is known from EP-A-0747406. In these known block polypropylenes there is a long isotactic block and few short syndiotactic blocks. A generically defined metallocene compound is disclosed as a catalyst component in the production of these block polypropylenes. The metallocene compound has a cyclopentadienyl ring which is monosubstituted, as exemplified by isopropylidene (3-trimethylsilylcyclopentadienyl-9-fluorenyl) zirconium dichloride and diphenylmethylenedibenzosilole (3-trimethylsilylcyclopentadienyl-9-fluorenyl) zirconium dichloride.

The production of syndiotactic/atactic block polyolefins is known from EP-A-0818475. In these known block polypropylenes there are alternating blocks of long syndiotactic and short atactic sequences. A generically defined metallocene compound is disclosed as a catalyst component in the production of these block polyolefins. The metallocene compound requires a heteroatom ligand coordinated to the metal of the metallocene, as exemplified by 2,7-bis-tert-butyl-fluorenyl-9-dimethylsilyl-tert-butyl-amido titanium dichloride.

In EP-A-0423101 and EP-A-0742227 a metallocene compound is described which has a lack of bi-lateral symmetry, one example of which is isopropylidene (3-methyl cyclopentadienyl-1-fluorenyl)zirconium dichloride. This compound was used in the production of hemiisotactic polypropylene. The structure of hemiisotactic polymers may be represented in a Fischer projection as follows:



The monomeric unit of the polymer is of the following structure:



wherein  $\text{R}_s$  is a hydrocarbyl group or nonhydrocarbyl group.

The structure of the polymer is characterised by  $\text{R}_s$  groups attached to every other asymmetric carbon atom being on the same side of the principal polymer chain as represented in a Fischer projection and  $\text{R}_s$  groups attached to the remaining asymmetric carbon atoms being either on the same side or the opposite side of the principal polymer chain. Since only every other one conforms to the isotactic structure, it is "hemi". The material is a noncrystalline polymer.

#### SUMMARY OF THE INVENTION

The present applicants have surprisingly found that short sequence syndiotactic/isotactic block polypropylenes can be prepared which have high clarity and elastomeric properties using an -aryl- substituted metallocene compound as a catalyst component.

The present invention provides a  $\text{C}_1$  symmetric metallocene compound of general formula  $\text{R}''(\text{CpR}_n)(\text{Cp}'\text{R}'_m)\text{MQ}_p$  for use as a catalyst component in the production of short sequence syndiotactic/isotactic block polyolefins, wherein  $\text{Cp}$  is a substituted cyclopentadienyl; each  $\text{R}$  is independently aryl or hydrocarbyl having 1 to 20 carbon atoms, at least position 3 of  $\text{Cp}$  is substituted with aryl, at least one other position of  $\text{Cp}$  is substituted with a non-bulky substituent, and  $n$  is an integer in the range from 2 to 4;  $\text{Cp}'$  is substituted or unsubstituted

fluorenyl; each R' is independently hydrocarbyl having 1 to 20 carbon atoms and m is 0 or an integer in the range from 1 to 8; R'' is a structural bridge to impart stereorigidity between Cp and Cp'; M is a metal from Group IIIB, IVB, VB or VIB; Q is a hydrocarbyl radical having 1 to 20 carbon atoms or a halogen; and p is the valence of M minus 2.

The polyolefin is preferably polypropylene. By short sequence syndiotactic/isotactic block polypropylene is meant a polypropylene that comprises alternating blocks of syndiotactic and isotactic sequence. Preferably, the average sequence length of each sequence is in the range 5 to 20, more preferably 5 to 10, most preferably around 6. The relative frequency of each sequence is typically in the range 1:3 to 3:1.

Preferably the isotactic and syndiotactic sequences have approximately the same length and frequency.

In the metallocene compound, the non-bulky substituent is preferably a linear hydrocarbyl having 1 to 20 carbon atoms, isobutyl or aryl. The non-bulky substituent should not interfere with the bridge and could be situated at position 2 and/or position 5, preferably at position 5. Cp is preferably substituted at position 3 of the ring with Ph.

The metal, M, is preferably Ti, Zr or Hf and Q is preferably a halogen, usually Cl. Typically R'' is alkylidene having 1 to 20 carbon atoms, a dialkyl germanium or silicon or siloxane, alkyl phosphine or amine, preferably a hydrocarbyl radical having at least one carbon atom to form the bridge. More preferably R'' is isopropylidene.

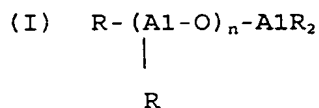
In a further aspect there is provided a catalyst system for use in preparing short sequence syndiotactic/isotactic block polyolefins, which comprises (a) a metallocene compound as defined above; and (b) a cocatalyst capable of activating the metallocene compound. Typically, the cocatalyst comprises an

- 5 -

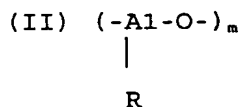
aluminium- or boron-containing cocatalyst.

Suitable aluminium-containing cocatalysts comprise an alumoxane, an alkyl aluminium and/or a Lewis acid.

The alumoxanes usable in the process of the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula:



for oligomeric, linear alumoxanes and



for oligomeric, cyclic alumoxane, wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

Suitable boron-containing cocatalysts may comprise a triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696, or those of the general formula [L'-H] + [B Ar<sub>1</sub> Ar<sub>2</sub> X<sub>3</sub> X<sub>4</sub>]- as described in EP-A-0277004 (page 6, line 30 to page 7, line 7).

The catalyst system may be employed in a solution polymerisation process, which is homogeneous, or a slurry process, which is heterogeneous. In a solution process, typical solvents include hydrocarbons with 4 to 7 carbon atoms such as heptane, toluene

or cyclohexane. In a slurry process it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins such as finely divided polyethylene.

Preferably, the support is a silica having a surface area comprised between 200 and 700 m<sup>2</sup>/g and a pore volume comprised between 0.5 and 4 ml/g.

The amount of alumoxane and metallocenes usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably the aluminium to transition metal mole ratio is in the range between 1:1 and 100:1, preferably in the range 5:1 and 50:1.

The order of addition of the metallocenes and alumoxane to the support material can vary. In accordance with a preferred embodiment of the present invention alumoxane dissolved in a suitable inert hydrocarbon solvent is added to the support material slurried in the same or other suitable hydrocarbon liquid and thereafter a mixture of the metallocene catalyst component is added to the slurry.

Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperature and which do not react with the individual ingredients. Illustrative

examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene.

Preferably the support material is slurried in toluene and the metallocene and alumoxane are dissolved in toluene prior to addition to the support material.

In a further aspect the present invention provides a process for preparing a short sequence syndiotactic/isotactic block polyolefin, which comprises contacting the catalyst system with at least one olefin in a reaction zone under polymerisation conditions.

In a further aspect there is provided a polypropylene comprising at least 10 alternating blocks of syndiotactic sequence and isotactic sequence, wherein the relative frequency of the sequences in the polypropylene is in the range 1:3 to 3:1, as determined by the ratio of mmmm pentads to rrrr pentads in <sup>13</sup>C NMR spectroscopy.

The invention will now be described in further detail, by way of example only, with reference to the following Examples and the accompanying drawings, in which:

FIGURE 1 shows in outline a reaction scheme for the production of isopropylidene(3-phenylcyclopentadienyl-9-fluorenyl)zirconium dichloride.

#### DETAILED DESCRIPTION OF THE INVENTION

##### Example 1

Synthesis of isopropylidene(3-methyl-5-phenylcyclopentadienyl-9-fluorenyl)zirconium dichloride

The synthesis is shown in outline in Figure 1. In a 500ml flask

equipped with a magnetic stirrer and a nitrogen inlet, 14.5 grams (87 mmole) of fluorene is dissolved in 140 ml of tetrahydrofuran (THF). At 0°C an equimolar amount of methyllithium (MeLi) in ether is added dropwise and the resulting red reaction mixture is stirred for 2h at ambient temperature. At 0°C an equimolar amount of 6,6-dimethyl-3-phenylcyclopentadienylfulvene in THF is added dropwise. The reaction mixture was stirred overnight at ambient temperature and hydrolysed with an aqueous, saturated solution of ammonium chloride in water. Subsequently the organic phase was separated with ether and dried over  $\text{MgSO}_4$ . The evaporation of the solvents yielded an offwhite solid (70% yield after recrystallization). 5.44g (15 mmole) of the ligand prepared above was dissolved in 100 milliliters of THF and treated with two equimolar quantities of MeLi in diethyl ether under nitrogen at 0°C. The red reaction mixture was stirred at ambient temperature overnight. After evaporation of THF a red powder was obtained that was washed with pentane. The powder was suspended in 200 milliliters of pentane and reacted with an equimolar amount of zirconium tetrachloride. A crude product was obtained which was dissolved in methylene chloride and filtered to separate the lithium chloride by-product. The methylene chloride is evaporated and the resulting solid washed with toluene until purely red (47% yield). The structure and composition were determined by  $^1\text{H}$  NMR.

## Example 2

### Polymerisation Procedure and Results

Propylene was polymerized using 1.8mg milligrams of isopropylidene(3-phenylcyclopentadienyl-9-fluorenyl) zirconium dichloride produced by the method above. One liter of liquid propylene was introduced into a Buechi reactor at room temperature. The catalyst was placed in three milliliters of 11% MAO in toluene to form a solution which was added to the reactor at 40°C and the temperature then increased to 60°C. The polymerization reaction was allowed to run for 60 minutes during which time the reactor was maintained at 60°C. The reaction was

terminated by venting the reactor of monomer. The catalyst activity in kilograms of polypropylene per grams of catalyst per hour was calculated. The molecular weight, molecular weight distribution, glass transition temperature and  $^{13}\text{C}$  NMR analysis of the polymer were determined.

A polypropylene was obtained at an hourly production rate of 60kg/g catalyst which had a number average molecular weight ( $M_n$ ) at 58528 Da, a weight average molecular weight ( $M_w$ ) of 136212 Da, a D value ( $M_w/M_n$ ) of 2.3 and a glass transition temperature of  $-3^\circ\text{C}$ .

Table 1 shows the results of microtacticity analysis from  $^{13}\text{C}$  NMR data in which the % of mmmm pentads is close to the % of rrrr pentads confirming the production of short sequence syndiotactic/isotactic polypropylene.

The length of stereoblocks can be estimated by the following formulae [Xu et al., Macromolecules, Vol.30, No.9, 1997, p.2539]:

The average sequence length of racemic units in long racemic sequences can be estimated as  $l(r) = 2[\text{rrrr}]/[\text{mrrr}] + 3$

Similarly, the average sequence length of meso units in long meso sequences can be estimated as  $l(m) = 2[\text{mmmm}]/[\text{mmmr}] + 3$

Applying these formulae to the data in Table 1 for the polymer from Example 2 this calculates to an average sequence length of racemic units of 6 and an average sequence length of meso units of likewise 6.

Table 1

**PENTADS**

Sequence	%
mmmm	19,82
mmmr	13,00
rmmr	6,00
mmrr	23,76
rmrr+mrmm	2,34
mrmm	1,02
rrrr	15,24
mrrr	11,30
mrrm	7,52

**TRIADS**

Sequence	%
mm	38,82
mr	27,12
rr	34,06

**DYADS**

Sequence	%
m	52,38
r	47,62

## CLAIMS:

1. A  $C_1$  symmetric metallocene compound of general formula  $R''(CpR_n)(Cp'R'_m)MQ_p$  for use as a catalyst component in the production of short sequence syndiotactic/isotactic block polyolefins, wherein Cp is a substituted cyclopentadienyl; each R is independently aryl or hydrocarbyl having 1 to 20 carbon atoms, at least position 3 of Cp is substituted with aryl, at least one other position of Cp is substituted with a non-bulky substituent, and n is an integer in the range from 2 to 4; Cp' is substituted or unsubstituted fluorenyl; each R' is independently hydrocarbyl having 1 to 20 carbon atoms and m is 0 or an integer in the range from 1 to 8; R'' is a structural bridge to impart stereorigidity between Cp and Cp'; M is a metal from Group IIIB, IVB, VB or VIB; Q is a hydrocarbyl radical having 1 to 20 carbon atoms or a halogen; and p is the valence of M minus 2.
2. A metallocene compound according to claim 1, wherein the non-bulky substituent is a linear hydrocarbyl having 1 to 20 carbon atoms, isobutyl or aryl.
3. A metallocene compound according to claim 1 or claim 2, wherein the non-bulky substituent is at position 5 of Cp.
4. A metallocene compound according to any one of claims 1 to 3, wherein Cp is substituted at position 3 with Ph.
5. A metallocene compound according to any one of the preceding claims, wherein M is Ti, Zr or Hf.
6. A metallocene compound according to any one of the preceding claims, wherein Q is Cl.
7. A metallocene compound according to any one of the preceding claims, wherein R'' is alkylidene having 1 to 20 carbon atoms, a dialkyl germanium or silicon or siloxane, alkyl phosphine or amine.

8. A metallocene compound according to claim 7, wherein R" is a hydrocarbyl radical having at least one carbon atom to form the bridge.
9. A metallocene compound according to claim 8, wherein R" is isopropylidene.
10. A metallocene compound according to claim 1, which is isopropylidene(3-methyl-5-phenylcyclopentadienyl-9-fluorenyl) zirconium dichloride.
11. Use of a metallocene compound according to any one of the preceding claims as a catalyst component in the production of a short sequence syndiotactic/isotactic block polyolefin.
12. A catalyst system for use in preparing short sequence syndiotactic/isotactic block polyolefins, which comprises (a) a metallocene compound according to any one of claims 1 to 10; and (b) a cocatalyst capable of activating the metallocene compound.
13. A catalyst system according to claim 12, wherein the cocatalyst comprises an aluminium- or boron-containing cocatalyst.
14. A process for preparing a short sequence syndiotactic/isotactic block polyolefin, which comprises contacting a catalyst system according to claim 12 or claim 13 with at least one olefin in a reaction zone under polymerisation conditions.
15. A process according to claim 14, wherein the olefin is propylene.
16. A process according to claim 14 or claim 15, wherein the polyolefin comprises alternating blocks of syndiotactic and isotactic sequence having an average sequence length in the range 5 to 20.

17. A process according to claim 16, wherein the relative frequency of each block is in the range 1:3 to 3:1, as determined by the ratio of mmmm pentads to rrrr pentads in <sup>13</sup>C NMR spectroscopy.
18. A polypropylene comprising at least 10 alternating blocks of syndiotactic sequence and isotactic sequence, wherein the relative frequency of the sequences in the polypropylene is in the range 1:3 to 3:1, as determined by the ratio of mmmm pentads to rrrr pentads in <sup>13</sup>C NMR spectroscopy.
19. A polypropylene according to claim 18, wherein the relative frequency of the sequences is approximately 1:1.
20. A polypropylene according to claim 18 or claim 19, wherein the syndiotactic and isotactic sequences each have an average sequence length in the range 5 to 20.
21. A polypropylene according to claim 20, wherein the average sequence length is in the range 5 to 10.

1 / 1

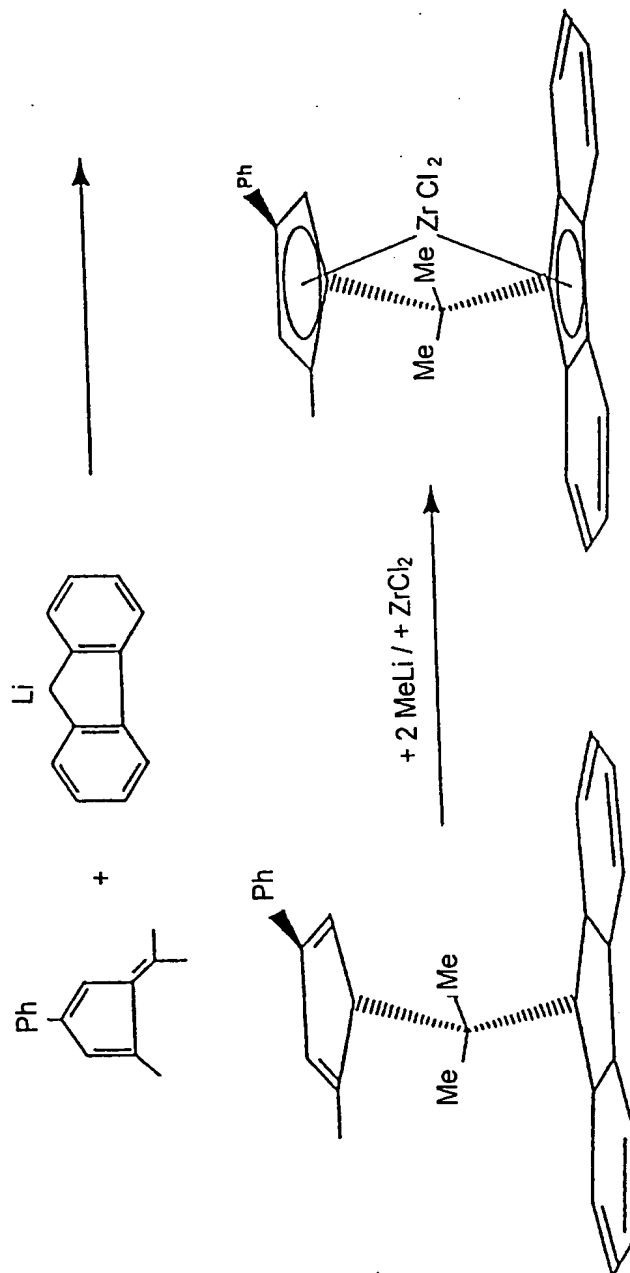


FIG. 1

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/04248

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C08F297/00 C08F297/06 C08F297/08 C08F10/00 C07F17/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08F C07F C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 747 406 A (FINA TECHNOLOGY) 11 December 1996 (1996-12-11) cited in the application	1-9, 11-21
Y	* page 3, line 20 ; page 3, line 14-50 ; page 4, line 37 - page 5, line 13 * page 6, line 31 -page 7, line 15	10
Y	EP 0 399 347 A (HOECHST AG) 28 November 1990 (1990-11-28) * page 3, line 1 - page 9, line 10 ; claims 1-2 ; example 2 *	10
Y	EP 0 742 227 A (FINA TECHNOLOGY) 13 November 1996 (1996-11-13) cited in the application * page 5, line 9-13 * page 4, line 17-26	1-21
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center;">30 September 1999</div>		Date of mailing of the international search report  <div style="text-align: center;">06/10/1999</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center;">Hammond, A</div>

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/04248

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 818 475 A (FINA RESEARCH)  14 January 1998 (1998-01-14)  cited in the application  * page 3, line 15 *  page 3, line 1-24  -----</p>	1-21

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/EP 99/04248

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0747406 A	11-12-1996	CA 2178411 A	08-12-1996
		DE 69600747 D	12-11-1998
		DE 69600747 T	08-04-1999
		ES 2123316 T	01-01-1999
		JP 9136930 A	27-05-1997
EP 0399347 A	28-11-1990	DE 3916553 A	22-11-1990
		AU 624953 B	25-06-1992
		AU 5577290 A	10-01-1991
		CA 2017192 A	20-11-1990
		DE 59010446 D	19-09-1996
		ES 2093003 T	16-12-1996
EP 0742227 A	13-11-1996	JP 3009913 A	17-01-1991
		US 5036034 A	30-07-1991
		CA 2027124 A	11-04-1991
		CN 1051735 A,B	29-05-1991
		CN 1100733 A	29-03-1995
EP 0818475 A	14-01-1998	EP 0423101 A	17-04-1991
		JP 3193796 A	23-08-1991
		AU 3939897 A	09-02-1998
		CA 2260891 A	22-01-1998
		WO 9802469 A	22-01-1998
		EP 0910591 A	28-04-1999
		NO 990073 A	08-01-1999